Condensation of Unsaturated Hydrocarbons with Phenols—Mechanism for the Condensation of the Ethylenic Bond with Phenols

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DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY AT NEW YORK UNIVERSITY

By

SAMUEL NATELSON

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CONDENSATION OF UNSATURATED HYDROCARBONS WITH PHENOLS—MECHANISM FOR THE CONDENSATION OF THE ETHYLENIC BOND WITH PHENOLS

Theoretical Part

Isolated cases of reactions between phenols and unsaturated compounds have been reported before. Isoprene,[1] cinnamic acid,[2] cyclohexene,[3] isoamylene, styrene[4] and acetylene[5] have been condensed with phenol type compounds under the influence of mineral acid with the formation of the corresponding substituted phenol in most cases.

In 1925 Niederl[6] showed that acetone condenses with phenols and that the resulting compounds could also be obtained by the interaction of unsaturated ketones with phenols. The reaction was shown to be an addition of the phenol to the unsaturated ketone.[7] This reaction was then systematically studied and it was found that the following types of unsaturated compounds would condense with phenols: alcohols,[8] ethers,[9] esters,[10] aldehydes,[11] ketones,[12] acids,[13] nitriles, amines, halides and ethylene oxide.[14]

The purpose of the present research was to continue the work on into the unsaturated hydrocarbon series in order to study the products obtained with a view toward a probable mechanism for all these condensation reactions with phenols.

β-Amylene and di-isobutylene were treated with phenol and the cresols in the presence of sulfuric acid. The corresponding ethers were obtained. The following mechanism is offered for this reaction, taking the reaction between β-amylene and *m*-cresol as an example.

It is first assumed that sulfuric acid is added to the unsaturation of amylene.[15] An ester would be formed of the structure

$$CH_3CH_2CH{=}CHCH_3 + H_2SO_4 = CH_3CH_2CH_2CH(CH_3)OSO_3H$$

Since condensation took place, it could only have taken place in one of two ways: either in the formation of a five carbon substituted phenol, or in an elimination of sulfuric acid with the formation of an amyl cresyl ether

$$CH_3CH_2CH_2CH(CH_3)\boxed{OSO_3H + H}OC_6H_4(CH_3) = CH_3CH_2CH_2CH(CH_3)OC_6H_4(CH_3)$$

This ether had not been reported in the literature up to this time and the proof of its structure was therefore undertaken. It was synthesized according to the Williamson method.[16] The resulting compound was shown to be identical with the ether obtained using the condensation method.

It appears from the work accomplished that the condensation of unsaturated ketones, alcohols, ethers, esters, aldehydes, acids and hydrocarbons (where the reactions are carried out at higher temperatures) takes

a different course than the condensation of unsaturated hydrocarbons with phenols in the cold, substituted phenols being obtained in the first case and ethers in the latter. An explanation was then sought which would harmonize these differences. Claisen[17] and others[18] have shown that alkyl phenyl ethers with a negative group in the alkyl radical are prone to rearrange upon heating or, more rapidly, in the presence of mineral acid or zinc chloride. The formation of substituted phenols upon condensation of unsaturated alcohols, ethers, esters, aldehydes, ketones and acids with phenols can now be better explained. Addition of sulfuric acid is first assumed and then elimination of the acid with the formation of an ether. Ethers of these types, as mentioned above, have been shown to rearrange rapidly, especially in the presence of mineral acids. Under the conditions of the experiment, therefore, the ether was not isolated, but the substituted phenol was obtained.

In the condensation of amylene and di-isobutylene with phenols in the cold, ethers were formed with a saturated alkyl group. These are known to be stable and will not rearrange except under unusual conditions. It was therefore of interest to see whether these long-chain ethers would rearrange at higher temperatures. This would explain the substituted phenols obtained by König and Schrauth, by condensing unsaturated hydrocarbons at higher temperatures. *o*-Cresyl di-isobutyl ether was therefore gently refluxed for five hours in the presence of a mixture of zinc chloride and hydrochloric acid. A crystalline solid was obtained which was shown to be di-isobutyl *o*-cresol

$$(CH_3)C_6H_4OC_8H_{17} \xrightarrow{\text{Rearrangement}} (CH_3)C_6H_3(C_8H_{17})OH$$

The mechanism then proposed for all these condensations of unsaturated compounds with phenols would constitute an addition of hydrogen sulfate to the ethylenic linkage and a subsequent elimination of the acid with the formation of an ether. This ether in the case of saturated alkyl chains is stable and will not rearrange. In the case of more negative or heavier groups, rearrangement takes place with the formation of the corresponding substituted phenol.

For the conclusive proof of the reaction mechanism offered in such condensations, it was necessary that it be shown that saturated alkyl phenyl ethers would rearrange under the conditions used by König. In all the ethers obtained (*sec.*-amyl phenyl and cresyl ethers; di-isobutyl phenyl and cresyl ethers) the oxygen is at a secondary or tertiary carbon atom. Since no data on the rearrangement of such types of compounds could be found in the literature, the simplest case, the various isopropyl phenyl and cresyl ethers, was then chosen for study.

There have been numerous cases of rearrangement already reported.[17,18]

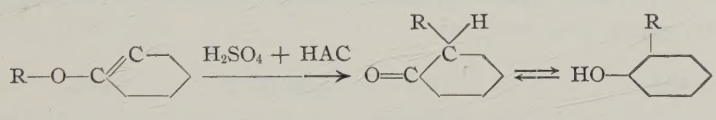
Where the alkyl group is a negative one, mere heat is necessary. As the alkyl group becomes less and less negative, various reagents, such as zinc chloride and hydrogen chloride, have to be used to effect rearrangement.

A mixture of concentrated sulfuric and glacial acetic acid should then be an excellent means for rearranging alkyl phenyl ethers. This reagent has the advantage of bringing the whole reaction mixture into homogeneous solution, while at the same time the concentration of the active rearranging agent, sulfuric acid can be reduced to any desired quantity. The ease with which the resultant product may be isolated is apparent, it only being necessary to add water to separate the rearranged product.

From the reactions studied there appears to be very little side reaction, the only product obtained other than the rearranged ether being the original ether itself, which can be again subjected to rearrangement.

The mechanism for this type of rearrangement as offered by Van Alphen involves oxonium formation. Kursanov suggests hydrolysis of the ether to the phenol and the alkyl halide and then recombination with the formation of a substituted phenol. Neither of these authors explains the rearrangement of alkyl ethers in the absence of a rearranging agent. Claisen's mechanism is a special one and requires the presence of the unsaturation in the alkyl residue. From Latimer's considerations,[19] the substituted phenol structure is a more stable configuration than that of the ether and therefore when placed in a suitable medium or under suitable conditions, readjustment to the more stable configuration should be expected.

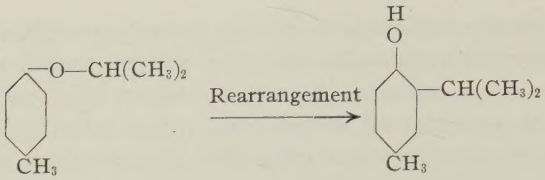
Drawing an analogy from keto–enol tautomerism and rearrangement of vinyl alkyl ethers to the corresponding aldehydes, the series of reactions may be represented as



As mentioned before, the ethers chosen for study were the isopropyl phenyl and cresyl ethers. Some of these ethers and the corresponding phenols obtained after rearrangement had not been previously prepared and had to be characterized.

The complete identification of the substituted phenols formed would involve determination of the position of the alkyl groups introduced. This would permit us to draw conclusions and generalizations which would be of great value in the identification and structure proof of a number of new longer chain phenols obtained by a similar process and to be described later.

The rearrangement of isopropyl *p*-cresyl ether was first studied. The reaction went smoothly and the rearranged phenol was isolated.

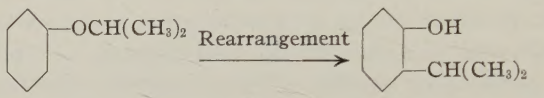


The isopropyl group could migrate to the ortho position only, the para position being occupied and meta rearrangement being rare.

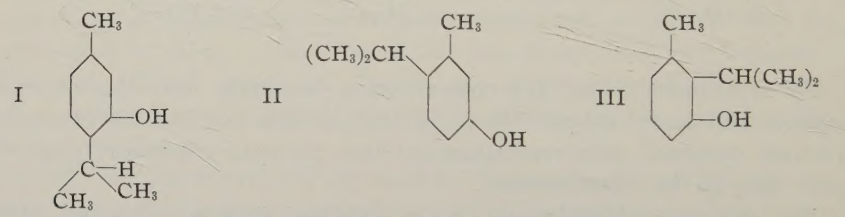
The rearrangement of isopropyl phenyl ether gave rise to a product the main portion of which distilled in the neighborhood of the boiling point of *o*-isopropyl phenol as reported in the literature.[20]

The product obtained on treating this product with bromoacetic acid was identical with that reported in the literature for *o*-isopropylphenoxy-acetic acid.[21]

The product therefore appears to be identical with *o*-isopropylphenol and the alkyl group in the ether has apparently migrated ortho to the hydroxyl group



It was expected that by the rearrangement of the isopropyl *m*-cresyl ether, thymol would be obtained. Actually a strong odor of thymol was observed, the total product boiling between 230–240°. From the fraction boiling between 231–235° a derivative with bromoacetic acid was made which melted 4° lower than that of thymol. According to Crum–Brown's rule there are three isomeric products possible upon the introduction of an isopropyl group into *m*-cresol.



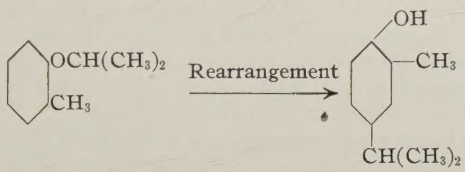
Thymol 3-Methyl-4-isopropylphenol 2-Isopropyl-3-methylphenol

Of these only I (thymol) has been identified conclusively. A condensation product furnished by Read[22] was studied and was found to be different from thymol and the rearranged isopropyl *m*-cresyl ether.

Usually upon treatment of an alcohol with phenol in the presence of a condensing agent the alkyl radical enters in a position para to the hydroxyl

group.[23] Structural Formula II may then be assigned to these types of products. The only possible structure for the substituted phenol obtained from isopropyl *m*-cresyl ether by the rearrangement process mentioned before, would then be Formula I or III, which would be in harmony with the fact observed that whenever the ortho positions are free migration to this place is preferred. Formula III would involve readjustment to a position which should be particularly non-reactive due to such phenomena as steric hindrance. A definite stand as to the position occupied is not being taken until the behavior of this compound is studied further.

The rearrangement of the *o*-cresyl isopropyl ether gave rise to a product which was identified by its physical and chemical properties and by its bromine derivative as *p*-isopropyl-*o*-methylphenol. The compound appears to be identical with that obtained by Kelbe and Spica,[24] the structure of which is given as



With a methyl group occupying an ortho position, migration para to the hydroxyl group appears to be favored.

This reaction was then applied to *sec.*-butyl, *sec.*-amyl and di-isobutyl ethers. In all cases rearrangement was observed. The di-isobutyl ethers rearranged on mere distillation, while normal amyl, butyl and propyl ethers did not rearrange. Di-isobutyl guaiacol was prepared by condensation and distillation.

Experimental Part

Condensation Method.—The method followed in these condensations is based upon work reported in earlier articles.[25]

One molecular weight of the cresol or phenol was weighed into a 500-cc. Erlenmeyer flask. To this was added one mole of the unsaturated hydrocarbon, care being taken to avoid excessive evaporation. The flask was well corked and the contents shaken until complete solution had taken place. The mixture was surrounded by an ice- and salt-bath and allowed to come to zero degrees. Ninety-eight grams of sulfuric acid was weighed out and transferred to a buret. Two drops of sulfuric acid were carefully added. The cork was replaced and the flask thoroughly shaken, keeping the whole immersed in the freezing mixture. The remaining sulfuric acid was then added drop by drop with constant stirring and shaking. At no time was the temperature allowed to go over zero degrees. If this precaution is not observed side reactions are favored and a marked decrease in the yield is noticed. After half of the sulfuric acid has been added further addition does not increase the temperature greatly and the remainder can be added fairly rapidly.

The flask was then stoppered with a cork through whose bore was placed a calcium chloride drying tube to exclude moisture and to allow any gases formed to escape. The mixture, which was almost colorless and mobile at first, turned a pink, brown or red color on standing, dependent upon the phenol or cresol used, and assumed a heavy viscous appearance. The flask was allowed to remain in the bath until the ice had melted, and then after shaking was allowed to stand for one week at room temperature with occasional shaking. The viscosity seemed to increase slowly until it reached a constant value after four or five days.

The mixture was loosened from the walls of the vessel with ice water. Five molar, ice cold, sodium hydroxide was then added until the whole solution was just alkaline. On standing an oil separated at the top of the liquid. This was removed in a separatory funnel. In some cases it was more convenient to extract with ether and then evaporate the ether on a water-bath.

The separate oil was washed twice with 50-cc. portions of dilute alkali (5%). It was then washed with two 50-cc. portions of saturated salt solution and then with 25 cc. of distilled water.

The liquid was dried over anhydrous potassium carbonate overnight, then transferred to an Erlenmeyer flask and a few bright pieces of sodium were introduced. After being left overnight effervescence ceased and the liquid was then distilled over a small piece of sodium. This precaution was necessary to remove the last traces of cresol or amyl alcohol, which may have been formed in the reaction as a by-product. The distillate thus obtained was then fractionated several times.

s-Amyl *m*-Cresyl Ether, 2-*m*-Cresoxypentane, $CH_3CH_2CH_2CH(CH_3)OC_6H_4(CH_3)$.—This compound was obtained by applying the above method to amylene (b. p. 35–37°) and *m*-cresol. The fraction first collected was between 210–245°. Upon redistillation most of the liquid came over between 235–238°. The material was a clear mobile liquid which had a faint aromatic odor: b. p. 238° (uncorr.); n_D^{21} 1.500; sp. gr. 0.920 (20°).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.89; H, 10.11; mol. wt. 178. Found: C, 80.57; H, 10.77; mol. wt. 179.6.

The above ether was nitrated, using the following method: 20 cc. of concentrated sulfuric acid was mixed with 1 cc. of the condensation product. Concentrated nitric acid was added drop by drop until the vigorous reaction had ceased; 5 cc. was added in excess and the whole warmed on a water-bath until brown fumes ceased to be given off.

The reaction mixture was then poured into 200 cc. of water, when a yellowish-brown precipitate came out on standing. The precipitate was washed with water, a limited quantity of dilute sodium bicarbonate solution and then again with small portions of water. The brown mass was dried on a porous plate and recrystallized from 75% alcohol.

The material on recrystallization gave dark brown needles melting at 106°, which was shown to be trinitro-*m*-cresol. This product is probably formed on hydrolysis of the ether by the sulfuric acid and then nitration of the freed cresol.

Anal. Calcd. for $C_7H_5N_3O_7$: N, 17.29. Found: N, 17.01.

s-Amyl *m*-cresyl ether was also prepared by the following method:[26] 14 g. of sodium was dissolved in 200 cc. of absolute ethyl alcohol in a three-necked flask fitted with a reflux condenser. While the last bit of sodium was dissolving, 65 g. of *m*-cresol was added through a dropping funnel. The whole was refluxed for twenty minutes. Through the same dropping funnel extending below the level of the liquid, amyl bromide prepared by the method of Wurtz[15] was added drop by drop with constant refluxing. After all the halide had been added, refluxing was continued for two hours more. Sodium bromide separated out in less thad twenty minutes and the flame had to be kept low to

avoid excessive bumping. At the end of two hours the flask was allowed to cool and its content filtered with suction from the separated sodium bromide. The filtrate was put in a distilling flask and the alcohol distilled off.

The oil was separated from more sodium bromide, which had come out, by extraction with ether. The ether extract was washed with dilute sodium hydroxide solution, then with water and dried over calcium chloride. It was next treated with metallic sodium to remove any alcohol or cresol still left. The ether was evaporated and the oil fractionated. The major portion came over between 234–238°: b. p. 238° (uncorr.); n_D^{21} 1.496; sp. gr. 0.915 (20°).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.89; H, 10.11. Found: C, 80.82; H, 10.11.

On nitrating, as described before, trinitro-*m*-cresol was also obtained.

By applying the procedure given for amylene and *m*-cresol to phenol and the other cresols the following products were obtained.

***s*-Amyl *p*-Cresyl Ether, 2-*p*-Cresoxypentane,** $CH_3CH_2CH_2CH(CH_3)OC_6H_4(CH_3)$.—The crude product distilled between 220–240°. This on careful redistillation gave a product which boiled fairly constantly between 223–225°; b. p. 225° (uncorr.); sp. gr. 0.920 (20°); n_D^{21} 1.505.

***s*-Amyl *o*-Cresyl Ether, 2-*o*-Cresoxypentane,** $CH_3CH_2CH_2CH(CH_3)OC_6H_4(CH_3)$.—The crude product distilled between 210–240°. On fractionation most of the material came over between 231–234°; b. p. 234°; n_D^{21} 1.493; sp. gr. 0.915 (20°).

The application of the condensation process to di-isobutylene, phenol and the cresols yielded the following products.

Di-isobutyl Phenyl Ether, 2,2,4-Trimethyl-4-phenoxypentane, $CH_3C(CH_3)_2CH_2C(CH_3)_2OC_6H_5$.—The material obtained was a clear, colorless liquid which solidified to needle-like crystals on prolonged cooling in an ice- and salt-bath. The material distilled with slight decomposition at atmospheric pressure. It distilled at 190° at 40 mm.; m. p. 12°; b. p. 258° (760 mm.); 190° (40 mm.); sp. gr. 0.950 (20°); n_D^{21} 1.510.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.55; H, 10.68. Found: C, 80.49; H, 10.47.

By applying the Williamson method to di-isobutyl bromide prepared by the method of Kondakow[27] and sodium phenolate, an ether was obtained which showed the following physical constants: m. p. 11°; b. p. 193° (40 mm.); n_D^{21} 1.505; sp. gr. 0.930 (20°).

On nitration of di-isobutyl phenyl ether after the method described under amyl-*m*-cresyl ether, a product was obtained which melted at 120° and was shown to be picric acid by a mixed melting point. This product was obtained from both the condensation product and the synthesized ether.

***p*-Cresyl Di-isobutyl Ether, 2,2,4-Trimethyl-4-*p*-cresoxypentane,** $CH_3C(CH_3)_2CH_2C(CH_3)_2OC_6H_4(CH_3)$.—A clear liquid was obtained which was purified by fractionation: b. p. 272° (uncorr.); n_D^{21} 1.470; sp. gr. 0.889 (20°).

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.82; H, 10.91. Found: C, 81.65; H, 10.91.

***m*-Cresyl Di-isobutyl Ether, 2,2,4-Trimethyl-4-*m*-cresoxypentane,** $CH_3C(CH_3)_2CH_2C(CH_3)_2OC_6H_4(CH_3)$.—The crude oil distilled from 250–275°. On fractionation the portion from 269–273° was collected; b. p. 273° (uncorr.); sp. gr. 0.895 (20°); n_D^{21} 1.476.

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.82; H, 10.91. Found: C, 81.99; H, 11.12.

Di-isobutyl *o*-Cresyl Ether, 2,2,4-Trimethyl-4-*o*-cresoxypentane, $CH_3C(CH_2)_3CH_2C(CH_3)_2OC_6H_4(CH_3)$.—B. p. 271° (uncorr.); m. p. 6° (uncorr.); sp. gr. 0.881 (20°); n_D^{21} 1.472.

Di-isobutyl *o*-Cresol $CH_3C(CH_3)_2CH_2C(CH_3)_2C_6H_3(CH_3)OH$.—Hydrogen chloride

was bubbled through 20 g. of di-isobutyl *o*-cresyl ether at zero degrees until 0.5 g. increase in weight was observed; 1 g. of anhydrous zinc chloride was added and the whole heated in an oil-bath to 200° for five hours. The mixture was steam distilled. An oil separated out which solidified to needle-like crystals on cooling. The phenolic properties of the compound are illustrated by its reaction with aqueous sodium hydroxide solution (formation of a soap-like sodium salt, soluble in water with difficulty) and of its alcoholic solution with ferric chloride with the formation of a transient green color; m. p. 49–50° (uncorr.).

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.82; H, 10.91. Found: C, 82.17; H, 10.37.

Preparation of Isopropylphenyl and Cresyl Ethers.—One molecular weight of the phenol or cresol was placed in a three-necked flask fitted with a reflux condenser. Fifty-eight grams (excess) of finely powdered potassium hydroxide was added and the whole heated with a low flame, when a homogeneous viscous mass is formed; 125 g. (excess) of isopropyl bromide was then slowly added through a dropping funnel extending below the level of the liquid. Constant warming was necessary to keep the whole mass from solidifying. After all the halide had been added refluxing was continued for two hours more. The mass was allowed to cool and then 500 cc. of water was added to dissolve the separated sodium bromide. A light oil appeared at the top of the liquid. This was removed in a separatory funnel and washed successively with 10% alkali and then twice with water. The separated light yellow oil was dried over calcium chloride and then distilled. One fractionation was sufficient to give a colorless constant boiling oil.

Rearrangement of Isopropylphenyl and Cresyl Ethers.—The rearrangement mixture consists of a solution of 150 cc. of concentrated sulfuric acid in sufficient glacial acetic acid to make up to a liter: 80 cc. of the ether prepared as above was placed in a flask fitted with a reflux condenser and a calcium chloride addition tube; 200 cc. of the rearrangement mixture was added and the whole shaken. Two layers are formed at first, but the mixture becomes homogeneous on warming. The solution was then refluxed gently for five hours. The temperature of the solution on refluxing is constant between 125–130°. The reaction mixture was then allowed to stand overnight. It assumed a deep red color. The whole was transferred to a 500-cc. separatory funnel and 200 cc. of water added. Sufficient solid hydrated sodium carbonate was added to neutralize the sulfuric acid (180 g.). The separatory funnel was then filled with a saturated salt solution. On standing, a heavy viscous oil separated to form the upper layer. The lower layer was allowed to drain off and discarded and the upper layer extracted with 10% potassium hydroxide solution. The alkali-insoluble portion was redistilled to reclaim unchanged ether. The alkali extract was neutralized with cold concentrated hydrochloric acid, ice being thrown in to keep the reaction mixture cool, when a deeply colored oil separated. The mixture was extracted with ether, the ether distilled off and the residue fractionated.

From 72 g. of ether, 39 g. of rearranged alkali-soluble product was obtained, and 16 g. of unchanged ether in the case of *m*-cresyl isopropyl ether. This corresponds to a 54% yield on the basis of the total ether at the outset, or a 70% yield taking into consideration the ether recovered.

Preparation of Isopropylphenoxy- and Cresoxyacetic Acids.—About one gram of the substituted phenol was weighed out carefully on an analytical balance. The exact quantity of 1 *N* potassium hydroxide was added and the whole gently warmed. A slight excess of bromoacetic acid was weighed into a separate flask and carefully neutralized with 1 *N* potassium hydroxide. The two solutions were mixed and then gently boiled for five minutes. Decolorizing charcoal was added and the whole filtered while hot. While still warm the calculated quantity of concentrated hydrochloric acid was

added and the mixture allowed to stand. The separated crystalline product was filtered off and recrystallized from hot water.

Isopropylphenyl Ether.[28]—A colorless oil with an odor resembling anise; b. p. 178°, sp. gr. 0.975 (20°), n_D^{20} 1.4992.

***o*-Isopropylphenol (2-Oxy-1-isopropylbenzene).**[7]—Colorless oil with phenolic odor, soluble in alkali. Its alcoholic solution gave a deep violet color with ferric chloride solution; b. p. 213–214°, sp. gr. 1.012 (20°), n_D^{20} 1.5315.

***o*-Isopropylphenoxyacetic Acid.**[8]—White needle-like crystals; soluble in hot water; m. p. 130° (uncorr.).

Anal. Calcd. for $C_9H_{12}O$: C, 68.04; H, 7.27; neut. equiv., 194. Found: C, 68.21; H, 7.62; neut. equiv., 200.

Isopropyl *o*-Cresyl Ether.—Light oil with a characteristic aromatic odor; b. p. 192° (uncorr.), sp. gr., 0.953 (20°), n_D^{20} 1.5040.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 80.15; H, 9.39.

6-Oxy-1-methyl-3-isopropylbenzene (2-Methyl-4-isopropylphenol).[11]—Colorless liquid with phenolic odor; b. p. 232–234° (uncorr.), sp. gr. 0.989 (20°), n_D^{20} 1.5178.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 80.29; H, 9.38.

(2-Methyl-4-isopropylphenoxy)-acetic Acid.—Prepared from the above compound by treating it with bromoacetic acid as described above; m. p. 87–88° (uncorr.).

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.23; H, 7.69; neut. equiv., 208. Found: C, 68.97; H, 7.46; neut. equiv., 203.

2,4,5-Tribromo-6-oxy-1-methyl-3-isopropylbenzene.[29]—Prepared by treating the 2-methyl-4-isopropylphenol in water with an excess of bromine. Upon recrystallization from alcohol lustrous, golden-yellow plates were obtained; m. p. 223° (uncorr.).

Isopropyl *m*-Cresyl Ether.—Faint pleasant aromatic odor; b. p. 195°, sp. gr. 0.931 (20°), n_D^{20} 1.4959.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 80.32; H, 8.95.

(3-Oxy-1-methyl-*x*-isopropylbenzene), 3-Methyl-*x*-isopropylphenol.—Odor strongly resembles that of thymol, alkali soluble. Its alcoholic solution was colored a deep lavender by ferric chloride solution; b. p. 230–235°, sp. gr. 0.994 (20°), n_D^{20} 1.5280.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 79.84; H, 9.39.

***x*-Isopropyl-*m*-cresoxyacetic Acid.**—Prepared from the above compound; small white crystals soluble in hot water; m. p. 141° (uncorr.).

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.23; H, 7.69; neut. equiv., 208. Found: C, 69.43; H, 7.85; neut. equiv., 213.

***y*-Isopropyl-*m*-cresoxyacetic Acid (3-Methyl-*y*-isopropylphenoxacetic Acid).**—This compound was prepared from a condensation product (b. p. 95–110° (4 mm.)),[22a] m. p. 125–126° (uncorr.).

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.23; H, 7.69; neut. equiv., 208. Found: C, 69.75; H, 7.36; neut. equiv., 209.

Isopropyl *p*-Cresyl Ether.—Strong disagreeable odor with a trace of anise; b. p. 195° (84°, 12 mm.), sp. gr. 0.927 (20°), n_D^{20} 1.4952.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 80.10; H, 9.39.

4-Oxy-1-methyl-3-isopropylbenzene (4-Methyl-2-isopropylphenol).—Characteristic odor, rather disagreeable; alkali soluble. Gives rise to a purple color with ferric chloride

in alcohol solution. In aqueous solution, a greenish turbidity is obtained with ferric chloride; b. p. 234–237° (uncorr.), sp. gr. 0.989 (20°), n_D^{20} 1.5277.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 79.80; H, 9.36.

(4-Methyl-2-isopropylphenoxy)-acetic Acid.—Long silky needles; soluble in hot water, difficultly soluble in the cold; m. p. 126° (uncorr.).

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.23; H, 7.69; neut. equiv., 208. Found: C, 69.43; H, 7.53; neut. equiv., 212.

Sec.-**Amyl *m*-Cresol.**—Colorless oil with an odor resembling thymol but much sweeter. Ferric chloride colors its alcoholic solution a wine red; b. p. 261° (uncorr.), sp. gr. 0.999 (22°), n_D^{22} 1.529.

(*Sec.*-**Amyl *m*-Cresoxy) Acetic Acid.**—Prepared from the above compound. Recrystallized from mixture of benzene and petroleum ether; m. p. 153°.

Sec.-**Butyl Phenyl Ether.**—Prepared by Williamson method; b. p. 185°, sp. gr. 0.976, n_D^{21} 1.5120.

Sec.-**Butyl Phenol.**—From rearrangement of above ether. A colorless oil which gave a violet color with ferric chloride in concentrated alcoholic solution; b. p. 220–225°, sp. gr. 1.011 (21°), n_D^{20} 1.5330.

Di-isobutyl Phenol.—Prepared by continuous distillation of the corresponding ether. No reaction with ferric chloride solution; m. p. 53°.

Di-isobutyl Guaiacol.—Prepared by condensation of diisobutylene with guaiacol and subsequent distillation; b. p. 141° (4 mm.), sp. gr. 0.983, n_D^{20} 1.5132.

Summary

The condensation of unsaturated hydrocarbons with phenolic type compounds was carried out. Ethers were obtained. This work, therefore, affords a method of preparing certain alkyl phenyl ethers.

A mechanism was proposed not only for this condensation reaction but also for all similar condensation reactions between compounds containing the ethylenic linkage and phenols in the presence of sulfuric acid.

Saturated alkyl phenyl ethers (isopropylphenyl and cresyl ethers) were rearranged to the corresponding substituted phenols by means of a mixture of concentrated sulfuric and glacial acetic acid. Proofs for the probable structure of the products obtained were advanced and a general rule as to the way of migration of the alkyl groups was given.

The reaction was applied to di-isobutyl, *sec.*-amyl, *sec.*- and tertiary butyl phenyl ethers.

This is the first instance of short chain.

Saturated alkyl phenyl ethers rearranging.

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